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In situ chemical oxidation of carbamazepine solutions using persulfate simultaneously activated by heat energy, UV light, Fe^{2+} ions, and H_2O_2

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ABSTRACT

In situ chemical oxidation of a carbamazepine solution was performed using persulfate anions simultaneously activated by heat energy (thermal, ultrasound), UV-C light, Fe^{2+} ions, and hydrogen peroxide. The main objective of this study was to analyze the mineralization reactions that occurred during the studied operating conditions. Solution TOC removal was nearly complete (99%) within 90 min, which prevented the accumulation of toxic intermediates. The mineralization process of carbamazepine solutions can be described using pseudo-second-order kinetics. Under acidic conditions, Fe^{2+} can exhibit catalytic effects on H_2O_2 decomposition and persulfate activation. With excess persulfate, an unproductive $S_2O_8^{2-}$ decomposition reaction (with no generation of $SO_4^{\bullet-}$) or a rapid reaction between excess sulfate radicals to produce sulfate anions could occur. Sulfate and hydroxyl radicals were involved in the main mineralization pathway. The influences of chloride ions on mineralization were also evaluated. The results demonstrated that this activated persulfate-based oxidation system could be used to control water pollution by emerging contaminants, such as carbamazepine.

1. Introduction

In recent years, the consumption of pharmaceutical products has considerably increased. This consumption has resulted in greater pharmaceutical concentrations in urban wastewater, surface water, drinking water, and hospital sewage [1–3]. These pollutants are not easily degraded by the conventional treatment processes used in wastewater treatment plants [4] and may have harmful effects on human health, aquatic species, and the environment. [5]. Carbamazepine is a pharmaceutical compound that is present in the aquatic environment [6–8] and is one of the most widely prescribed dibenzazepine derivatives. Apart from its common use for treating epilepsy, carbamazepine is administered for neuropathic pain and as therapy for manic episodes and bipolar effective disorders [9]. The percentage of carbamazepine removal in effluents from wastewater treatment plants is approximately 10% [10], and carbamazepine is bioaccumulated through food contamination in aquatic environments [11]. Therefore, an efficient treatment system for removing carbamazepine or its oxidation reaction intermediates from the aquatic environment is needed.

Advanced oxidation processes (AOPs) are effective methods for treating pharmaceutical pollutants. The efficiencies of AOPSs are based on the generation of highly reactive free radicals, especially hydroxyl radicals ($^{\bullet}OH$, $E_0 = 2.8$ V), by various combinations of processes, such as UV/H_2O_2, Fenton, photo-Fenton, UV/TiO_2, UV/O_3, or any combination of these with ultrasound. Recently, persulfate anions ($S_2O_8^{2-}$, $E_0 = 2.01$ V) have received attention as a potentially viable alternative for degrading recalcitrant or hazardous compounds. Due to its aqueous solubility, relatively high stability and low cost, persulfate can be used as a source of an even stronger oxidant, sulfate radicals ($SO_4^{\bullet-}$, $E_0 = 2.6$ V). Persulfate can be activated by heat (thermal, ultrasound), UV-C light, transition metal ions, or H_2O_2 [12–16].

Carbamazepine degradation has been investigated in many oxidative treatment processes, such as ozonation [17], direct photolysis [18], UV/H_2O_2 [19,20], UV/peroxymonosulfate [20], the photo-Fenton reaction [21], the photo-Fenton like reaction [22], TiO_2-assisted photocatalytic degradation [23], sonolysis [24], ultrasonic/Fenton treatment [25,26], and sonophotocatalysis with TiO_2 [27]. However, to the best of our knowledge, only limited information is available regarding the treatment of carbamazepine solutions using persulfate-based oxidation systems. Only four author groups have reported data regarding combinations of these processes. Specifically, carbamazepine degradation using an UV/persulfate process in an aqueous solution [20,28], thermally

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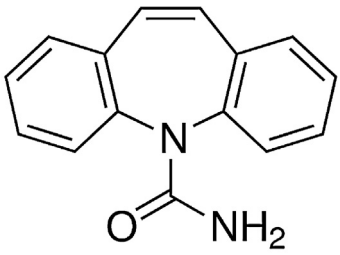

Molecular formula: $C_{15}H_{12}N_2O$

Molecular weight: 236.27 g mol^{-1}

Water solubility: 17.7 mg L^{-1} (20 ºC)

Fig. 1. Structure and properties of carbamazepine.

activated persulfate [29], the persulfate-assisted solar photo-Fenton like reaction [30] and a Fe^{2+}-activated persulfate process [31] have been reported.

This study is novel, because it analyzes the mineralization reactions of carbamazepine solutions by using persulfate simultaneously activated by heat energy (thermal, ultrasound), UV-C light, Fe^{2+} ions, and H_2O_2. First, the synergistic effects of binary systems using $S_2O_8^{2-}$ were evaluated. Next, mineralization reactions were conducted using the simultaneous persulfate activators. Finally, the reaction kinetics, sulfate and hydroxyl radical contributions, and the effects of chloride ions on the mineralization reaction were determined.

2. Experimental

2.1. Materials

Carbamazepine, $C_{15}H_{12}N_2O$ (Fig. 1) (purity 99%), and methanol were obtained from Sigma–Aldrich, and $FeSO_4{\cdot}7H_2O$, sodium persulfate ($Na_2S_2O_8$, 98%), and *tert*-butyl alcohol were purchased from Panreac. Hydrogen peroxide (30% w/v) and NaCl salt were obtained from Merck. All chemicals were used as received without further purification. The pH of the wastewater in each test was adjusted using H_2SO_4 and NaOH solutions.

The initial carbamazepine and total organic carbon (TOC) concentrations in the solutions were 15 and 14 mg L^{-1}, respectively. The aqueous solution was prepared using tap water (TOC: 2.6 mg L^{-1}).

2.2. Experimental runs

Fig. 2 illustrates the scheme of the experimental set-up. The loop set-up consists of a 50 L reservoir equipped with a sample port. The loop set-up was connected to the suction side of a centrifugal pump (130 W, Pan World Co., Ltd., model NH-100PX-X). The reaction was conducted using recirculation flow-through ultrasonic and UV-C reactors at a flow rate of 70 L min^{-1}. An ultrasonic processor UIP1000HD (1000 W, 20 kHz) consisting of a transducer and generator with automatic frequency tuning, an adjustable amplitude (25 μ) of 20–100% and a titanium horn (Hielscher Ultrasonics, Gmbh) was used to generate ultrasonic sound waves. This installation also included a photochemical reactor with four 280–200 nm UV-C lamps (TUV_TL_D_55W_HO_SLV UV-C PHILIPS). The UV-radiation intensity of the UV-lamps was measured using potassium ferrioxalate [32] and was 7.81×10^{-6} Einstein s^{-1}. A circulating water bath with a thermostat (Frigiterm 10, Selecta) was used to maintain a constant reaction temperature. During a typical run, the freshly aqueous carbamazepine solution was prepared in a tank containing 33 L of tap water and 495 mg of carbamazepine. The carbamazepine was solubilized using an electronic stirrer (RZR 2051 Heidolph, 100 rpm) at 40 °C for 4 h. Next, the solution containing carbamazepine was treated under different oxidation systems. For the duration of the tests, the samples were periodically withdrawn from the reactor to obtain the residual carbamazepine concentrations, total organic carbon, ferrous iron, hydrogen peroxide, and dissolved oxygen.

Sulfate and hydroxyl radical scavenging was accomplished using 10 mM *tert*-butyl alcohol or methanol to determine the contributions of the radical reactions to mineralization. Before analysis, all samples were withdrawn from the reactor to determine their H_2O_2 contents and were immediately treated with excess Na_2SO_3 (in solution) to prevent further oxidation (this procedure was performed to avoid overestimating degradation).

2.3. Analysis

The carbamazepine concentration was determined using high-performance liquid chromatography with UV detection (Agilent Technologies 1100 HPLC-UV) in the isocratic mode immediately after sampling. An Eclipse XDB-C18 column (5 μm, 4.6 × 250 mm) was used, and a 60:40 (v/v) methanol/(water with 0.1% acetic acid) mixture with an acidic pH was used as the mobile phase (detection wavelength, λ = 286 nm; flow rate of 0.6 mL min^{-1}). The mineralization grade of the treated wastewater was determined using a TOC analyzer (TOC-5050 Shimadzu, standard deviation < 0.2 mg L^{-1}). The H_2O_2 concentration in solution was determined by titration with an aqueous potassium permanganate (0.02 M) solution by using an automatic Titrino SET/MET 702 (Metrohm). The concentrations of the soluble iron species during the mineralization reaction were measured spectrophotometrically using the 1,10-phenanthroline method (according to ISO 6332) and a UV–vis spectrophotometer (HACH LANGE). The residual $S_2O_8^{2-}$ concentrations in the presence of iron were determined based on the methods of Liang et al. [33].

3. Results and discussion

3.1. Binary oxidation systems based on activated persulfate

First, the activation of the persulfate anion by using different systems was examined. The $S_2O_8^{2-}$/ultrasound (US), $S_2O_8^{2-}$/UV-C, $S_2O_8^{2-}/Fe^{2+}$, and $S_2O_8^{2-}/H_2O_2$ systems were used to degrade 15 mg L^{-1} of the carbamazepine solution (initial solution TOC content = 14 mg L^{-1}). The following experimental conditions were used: $[TOC]_0$ = 14 mg L^{-1}; $[Fe^{2+}]_0$ = 5 mg L^{-1}; $[H_2O_2]_0$ = 100 mg L^{-1}; $[S_2O_8^{2-}]_0$ = 300 mg L^{-1}; pH 2.8; temperature = 25 °C; ultrasound amplitude = 100%; and UV-radiation intensity = 7.81×10^{-6} Einstein s^{-1}. The reaction time was 120 min in all experiments.

Fig. 3 shows the TOC removal percentage as a function of reaction time for the single systems (US, UV-C, Fe^{2+}, H_2O_2, and $S_2O_8^{2-}$) and the four binary oxidation systems ($S_2O_8^{2-}$/US, $S_2O_8^{2-}$/UV-C, $S_2O_8^{2-}/Fe^{2+}$, and $S_2O_8^{2-}/H_2O_2$). The persulfate anion alone insignificantly affects the mineralization of the carbamazepine solution (%TOC removal = 0.5%). However, the TOC removal percentage increased when using the binary systems due to the generation of sulfate radicals from $S_2O_8^{2-}$ activation. This activation results from the homolysis of the peroxide bond by ultrasound or UV light or from a redox reaction involving Fe^{2+} or H_2O_2. In addition, Fig. 3 shows that the mineralization of carbamazepine solutions via single systems, such as Fe^{2+} (%TOC removal = 3.4%) or hydrogen peroxide systems (%TOC removal = 1.4%), was very inefficient. When only Fe^{2+} (Fig. 3c) was introduced into the carbamazepine solution, the small degree of mineralization achieved

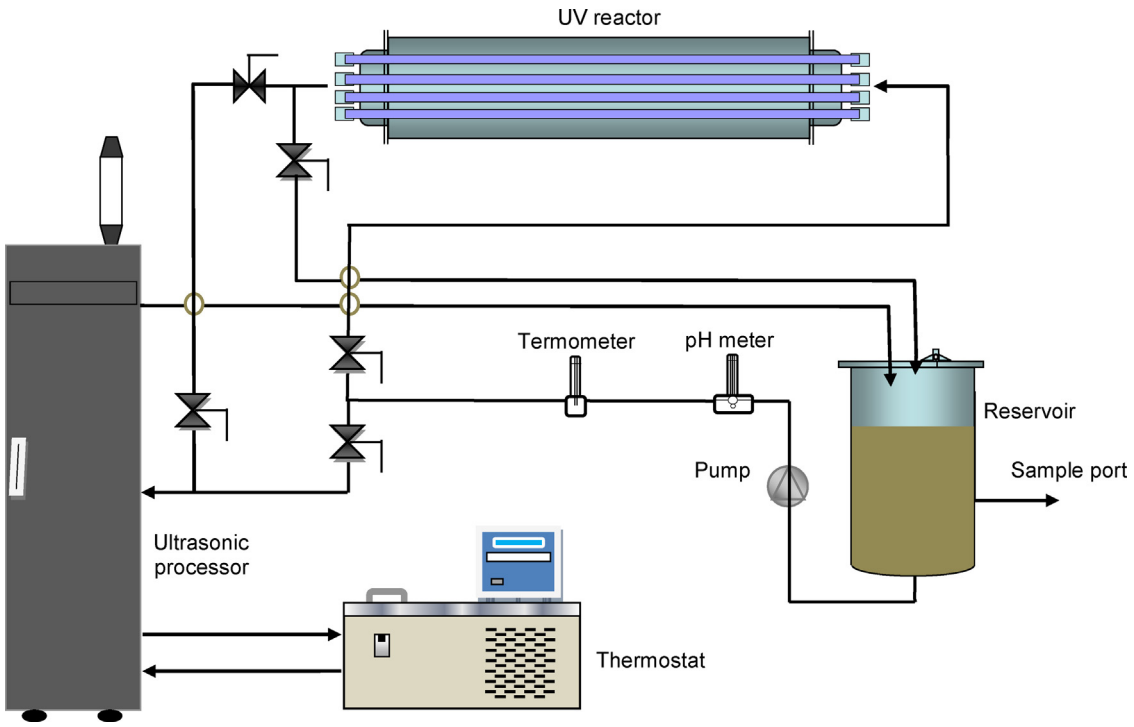

Fig. 2. Schematic illustration of the experimental set-up.

in this system could be attributed to the formation of small quantities of oxidative intermediate species, such as superoxide ($O_2^{\bullet-}$, according to Eq. (1)), hydrogen peroxide, and hydroxyl radicals (generated according to Eqs. (2) and (3), respectively) [34,35].

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet-} \quad (1)$$

$$Fe^{2+} + O_2^{\bullet-} + 2H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad (3)$$

The results shown in Fig. 3 confirmed that H_2O_2 and $S_2O_8^{2-}$ had negligible effects as single oxidants, indicating that the direct or molecular reactions between peroxide or persulfate and the possible compounds present in the carbamazepine solution did not occur or had slow oxidative kinetics.

By contrast, when the carbamazepine solution was treated using ultrasonic irradiation alone (Fig. 3a), the degree of mineralization was approximately 15% within 120 min of reaction. The ultrasonic process was conducted using the maximum power (amplitude) (100% amplitude, 450 W ultrasonic power, as quoted by the manufacturer) because preliminary experiments showed that the mineralization efficiency increased as the ultrasound amplitude increased from 20 to 100% (data not shown). This increase could be attributed to the generation of greater amounts of highly reactive radical species, such as hydroxyl ($HO^{\bullet}$), hydrogen ($H^{\bullet}$), and hydroperoxyl ($HO_2^{\bullet}$), at higher power intensities due to a greater number of cavitation bubbles. Although these radical species could be produced by the sonolysis of water according to Eqs. (4)–(9) [36], they are most likely not produced in sufficient quantities to achieve a high degree of mineralization.

$$H_2O +))) (\text{ultrasound}) \rightarrow HO^{\bullet} + H^{\bullet} \quad (4)$$

$$HO^{\bullet} + H^{\bullet} \rightarrow H_2O \quad (5)$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \quad (6)$$

$$2HO^{\bullet} \rightarrow H_2O_2 \quad (7)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H^{\bullet} + H_2O_2 \rightarrow HO^{\bullet} + H_2O \quad (9)$$

As shown in Fig. 3b, the degree of mineralization achieved by direct photolysis (UV-C alone) was only 15% because the carbamazepine quantum yield was only 2.3×10^{-3} mol E^{-1} [37].

Fig. 3a shows that the degree of mineralization significantly increased when using persulfate activated with ultrasound (%TOC removal = 26.4%) relative to the single systems. The greater observed TOC removal was attributed to the generation of sulfate radicals when the persulfate was activated with heat from the ultrasound cavitation (as shown in Eq. (10)) [13]. A small amount of hydroxyl radicals could be generated from sulfate radicals according to Eq. (11) [38]. Furthermore, ultrasonic irradiation can cause a strong mechanical effect in a homogeneous system and enhance the mass transfer reaction in solution.

$$S_2O_8^{2-} +))) (\text{ultrasound}) \rightarrow 2SO_4^{\bullet-} \quad (10)$$

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + H^+ + SO_4^{2-} \quad (11)$$

Combined treatment with UV-C irradiation and persulfate (Fig. 3b) enhanced the mineralization efficiency of the carbamazepine solution relative to the single systems. Overall, 21.4% of the initial TOC was removed within 120 min. In this case, persulfate was activated by 254 nm UV-C light (according to Eq. (12)) producing sulfate radicals [39]. In addition, a small amount of $HO^{\bullet}$ radicals was likely generated as indicated above.

$$S_2O_8^{2-} + h\upsilon \rightarrow 2SO_4^{\bullet-} \quad (12)$$

Fig. 3c shows the %TOC removal of the carbamazepine solution as a function of time when the $S_2O_8^{2-}/Fe^{2+}$ system was used. In this case, the mineralization efficiency (16%) increased considerably over of the single systems (%TOC removal: 1.4 and 3.4%, respectively, as indicated above). Fe^{2+} would be able to activate persulfate according to Eq. (13), which generates sulfate radicals and, most likely, $HO^{\bullet}$, as indicated above. The hydrolysis of $S_2O_8^{2-}$ under acidic conditions could generate H_2O_2 (Eq. (14)) and result in

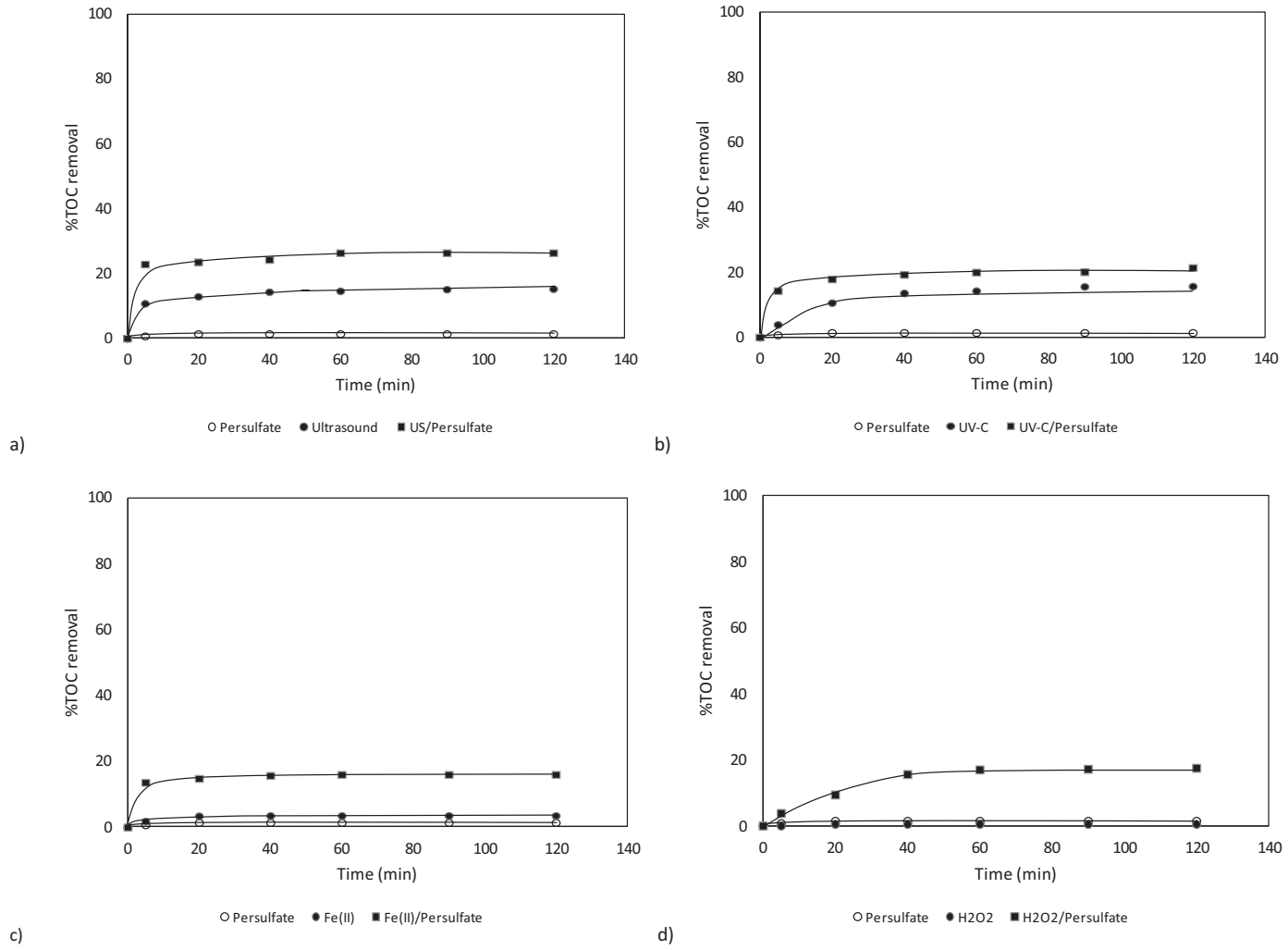

Fig. 3. Mineralization of the carbamazepine solution under different single and combined binary systems. Comparative study: (a) US/persulfate system; (b) UV-C/persulfate system; (c) Fe^{2+}/persulfate system; and (d) H_2O_2/persulfate system. Experimental conditions: $[TOC]_0 = 14\,mg\,L^{-1}$; $[Fe^{2+}]_0 = 5\,mg\,L^{-1}$; $[H_2O_2]_0 = 100\,mg\,L^{-1}$; $[S_2O_8^{2-}]_0 = 300\,mg\,L^{-1}$; pH 2.8; temperature = 25 °C; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81×10^{-6} Einstein s^{-1}.

Table 1
Activated persulfate-based processes. Synergistic effect.

Single system	%TOC removal	Combined system	%TOC removal	Synergy (%)
US	15.3	PS/US	26.4	36.74
UV-C	15.7	PS/UV-C	21.4	20.09
Fe^{2+}	3.4	PS/Fe^{2+}	16.0	70.00
H_2O_2	0.5	PS/H_2O_2	17.5	89.14
$S_2O_8^{2-}$	1.4	$S_2O_8^{2-}$/Fe^{2+}/UV/US	76.4	54.31
		$S_2O_8^{2-}$/Fe^{2+}/UV/H_2O_2	82.9	74.66
		$S_2O_8^{2-}$/Fe^{2+}/UV/US/H_2O_2	87.7	58.60

$[TOC]_0 = 14\,mg\,L^{-1}$; $[Fe^{2+}]_0 = 5\,mg\,L^{-1}$; $[H_2O_2]_0 = 100\,mg\,L^{-1}$; $[S_2O_8^{2-}]_0 = 300\,mg\,L^{-1}$; pH 2.8; temperature = 25 °C; ultrasound amplitude = 100%; UV-radiation intensity = 7.81×10^{-6} Einstein s^{-1}.

the Fenton reaction in the presence of Fe^{2+} (Eq. (15)), which would generate extra hydroxyl radicals [34].

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (13)$$

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^{-} + H_2O_2 \quad (14)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (15)$$

Fig. 3d shows that the degree of mineralization was greater in the combined $S_2O_8^{2-}/H_2O_2$ process than in the single systems. A TOC removal of 17.5% was achieved within 120 min of reaction. In this system, hydrogen peroxide reacts with persulfate to form sulfate and hydroxyl radicals, as shown in Eq. (16) [40].

$$S_2O_8^{2-} + H_2O_2 \rightarrow 2SO_4^{\bullet -} + 2HO^{\bullet} \quad (16)$$

A synergistic effect was concluded to occur between the single persulfate system and the other single systems (US, UV-C, Fe^{2+}, and H_2O_2). Thus, the oxidation processes using persulfate with addition of Fe^{2+} and H_2O_2 or US and UV-C significantly increased the TOC removal relative to the individual systems. The synergism (Sy (%)) was quantified using the TOC removal percentage according to Eq. (17) [41]. Table 1 shows the synergism values obtained for the

four binary systems under the studied operating conditions, which confirmed the existence of a synergistic effect.

$$Sy(\%) = \frac{\%TOCremoval(persulfate - basedcombinedprocess) - \sum \%TOCremoval(singlesystems)}{\%TOCremoval(persulfate - basedcombinedprocess)} \times 100 \quad (17)$$

Fig. 4 shows the evolution of the persulfate concentrations during the reactions in the four binary systems ($S_2O_8^{2-}$/US, $S_2O_8^{2-}$/UV-C, $S_2O_8^{2-}/Fe^{2+}$, and $S_2O_8^{2-}/H_2O_2$). The abatement of the initial $S_2O_8^{2-}$ concentration in the $S_2O_8^{2-}$/UV-C system was greater than that in the other three binary systems. This finding could indicate a higher production of sulfate radicals in the $S_2O_8^{2-}$/UV-C system. However, the synergistic effect was higher in the systems that used persulfate activated with Fe^{2+} or H_2O_2. This result potentially occurred because the $S_2O_8^{2-}$ was activated more quickly with UV-C light (see Fig. 4) and a $SO_4^{\bullet-}$ recombination and a reaction with persulfate could occur as shown in Eqs. (18) and (19), respectively [42]. Thus, the available $SO_4^{\bullet-}$ radical concentration for degrading TOC in solution decreased.

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (18)$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \quad (19)$$

Although the decomposition of $S_2O_8^{2-}$ was similar in the other three binary systems, the higher synergistic effect corresponded with the $S_2O_8^{2-}/H_2O_2$ system, where extra $HO^{\bullet}$ radicals (stronger oxidant) could be directly formed by Eq. (16). In this system, the amount of H_2O_2 consumed was 11 mg L^{-1} (0.32 mM) similar to the consumption of $S_2O_8^{2-}$ (79 mg L^{-1}; 0.33 mM).

3.2. Simultaneous activation of persulfate by US, UV-C, Fe^{2+}, and H_2O_2

Fig. 5a shows the evolution of the degree of carbamazepine mineralization in solution in the different activated persulfate-based oxidation systems. The values of the reaction parameters (temperature, pH, ultrasound, and UV-C and the initial concentrations of persulfate, ferrous iron, and hydrogen peroxide) were identical to the values used in single or combined systems indicated above. In the $S_2O_8^{2-}/Fe^{2+}$ reaction, the TOC removal occurred during the first 10 min until Fe^{2+} was fully oxidized to Fe^{3+}, likely because Fe^{3+} does not activate persulfate [43]. Various Ferric oxyhydroxides could be formed through hydrolysis according to Eqs. (20)–(22) [44]. At pH ≤ 3, $FeOH^{2+}$ is the dominant species in the solution. Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^{+}$ have lower efficiencies than Fe^{2+} for activating $S_2O_8^{2-}$ to create sulfate radicals.

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \quad (20)$$

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^{+} + 2H^+ \quad (21)$$

$$2Fe^{3+} + 2H_2O \rightarrow Fe_2(OH)_2^{4+} + 2H^+ \quad (22)$$

As expected, Fig. 5a shows that the TOC removal percentage increased as follows when persulfate was combined with Fe^{2+}, ultrasound, UV-C and H_2O_2: ($S_2O_8^{2-}/Fe^{2+}$/UV-C/US) system, TOC removal: 76.4%, synergistic effect = 54.31% (Table 1); ($S_2O_8^{2-}/Fe^{2+}$/UV-C/H_2O_2) system, TOC removal: 82.9%, synergistic effect = 74.66% (Table 1); and ($S_2O_8^{2-}/Fe^{2+}$/UV-C/US/H_2O_2) system, TOC removal: 87.7%, synergistic effect = 58.60% (Table 1). It is likely that the sulfate electrolyte (added as $FeSO_4 \cdot 7H_2O$) would increase the bubble potential and so the electrostatic repulsion between them. It would inhibit the coalescence of cavitation bubbles and would increase the number of them in the medium and con-

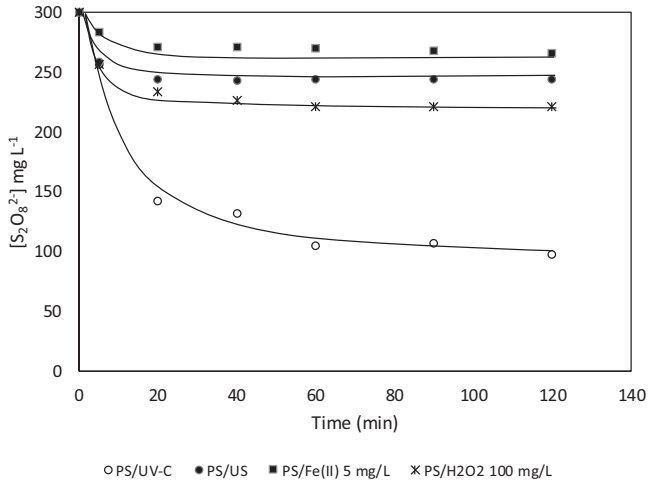

Fig. 4. Variations of the persulfate concentration over time in different binary systems. Experimental conditions: $[TOC]_0$ = 14 mg L^{-1}; $[Fe^{2+}]_0$ = 5 and 15 mg L^{-1}; $[H_2O_2]_0$ = 100 mg L^{-1}; $[S_2O_8^{2-}]_0$ = 300 mg L^{-1}; pH 2.8; temperature = 25 °C; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81 × 10^{-6} Einstein s^{-1}.

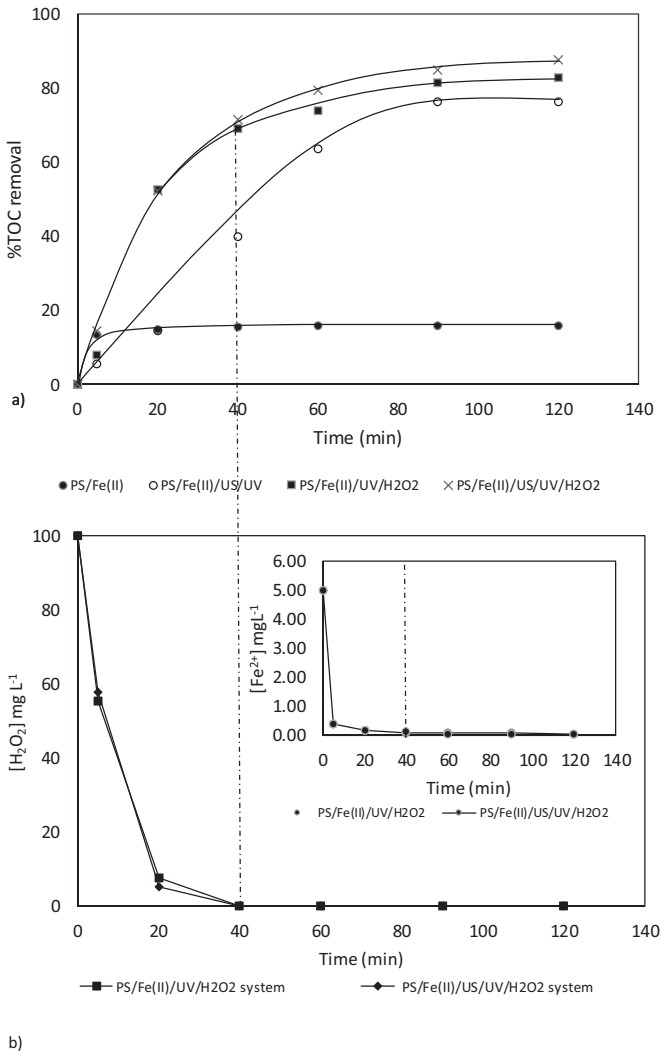

Fig. 5. Evolution of the degree of mineralization (%) and the hydrogen peroxide and ferrous ion concentrations over time in different degradation systems. Experimental conditions: $[TOC]_0$ = 14 mg L^{-1}; $[Fe^{2+}]_0$ = 5 mg L^{-1}; $[H_2O_2]_0$ = 100 mg L^{-1}; $[S_2O_8^{2-}]_0$ = 300 mg L^{-1}; pH 2.8; temperature = 25 °C; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81 × 10^{-6} Einstein s^{-1}.

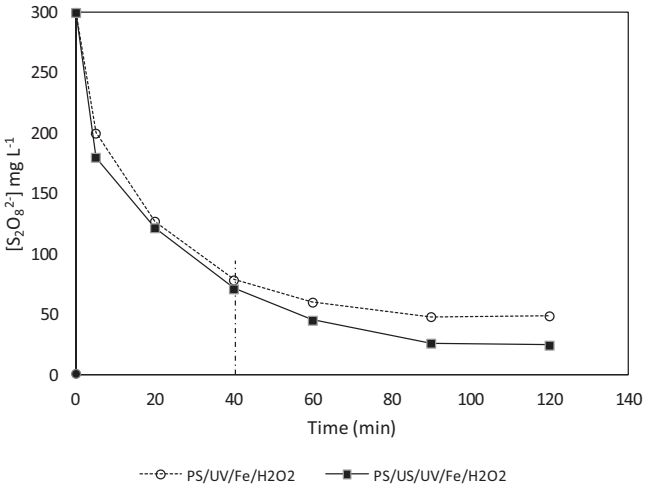

Fig. 6. Variations of the persulfate concentration over time in different systems. Experimental conditions: $[TOC]_0 = 14\,mg\,L^{-1}$; $[Fe^{2+}]_0 = 5$ and $15\,mg\,L^{-1}$; $[H_2O_2]_0 = 100\,mg\,L^{-1}$; $[S_2O_8^{2-}]_0 = 300\,mg\,L^{-1}$; pH 2.8; temperature = 25 °C; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81×10^{-6} Einstein s^{-1}.

sequently this effect will improve the radical production, which agrees with the findings of other authors [36]. Thus, the concentrations of sulfate radicals formed through sono-ferrous-activated persulfate would increase. In addition, Fe^{2+} would be regenerated through complex photo-reduction of $Fe(OH)^{2+}$, and extra hydroxyl radicals could be formed during the photo-Fenton reaction (UV-C/Fe^{2+}/H_2O_2) [45]. By contrast, under acidic conditions, Fe^{2+} can exhibit a catalytic effect on H_2O_2 decomposition (generating $HO^{\bullet}$) and persulfate activation. Thus, the system using persulfate and simultaneously activated by US, UV-C, Fe^{2+}, and H_2O_2 was the most efficient. As shown in Fig. 5a, the mineralization reaction rates in both systems ($S_2O_8^{2-}$/Fe^{2+}/UV-C/H_2O_2 and $S_2O_8^{2-}$/Fe^{2+}/US/UV-C/H_2O_2) were similar until 40 min of reaction, when hydrogen peroxide and ferrous ions disappeared (see Fig. 5b). Beyond 40 min, a higher mineralization degree was observed in the system combined with ultrasound. This result can be justified by considering Fig. 6, which shows similar persulfate decomposition in both systems until 40 min and a higher activation beyond 40 min in the ultrasound-assisted combined system, which indicates the generation of more sulfate radicals.

3.3. Kinetic study of the $S_2O_8^{2-}$/US/UV-C/Fe^{2+}/H_2O_2 reaction

To investigate the TOC removal rate of the carbamazepine solution using persulfate simultaneously activated by US, UV-C, Fe^{2+}, and H_2O_2, the mineralization results obtained at different temperatures were evaluated using the pseudo-second-order kinetic model with respect to the TOC concentrations, as shown in Eq. (23).

$$r_{TOC} = -\frac{d[TOC]}{dt} = k_{TOC}[TOC]^2 \quad (23)$$

where "r_{TOC}" is the mineralization reaction rate, "[TOC]" is the total organic carbon ($mg\,L^{-1}$) concentration at a given time "t" (min) and "k_{TOC}" is the pseudo-second-order kinetic rate constant ($L\,mg^{-1}\,min^{-1}$). This equation can be integrated between $t = 0$ and $t = t$ to yield the following equation:

$$\frac{1}{[TOC]} = k_{TOC}t + \frac{1}{[TOC]_0} \quad (24)$$

where $[TOC]_0$ is the initial TOC concentration. According to this expression, a plot of the first term versus "t" must yield a straight line with a slope of k_{TOC} to validate Eq. (24). As shown in Fig. 7a, a plot of 1/[TOC] against "t" provides a graph with a straight line

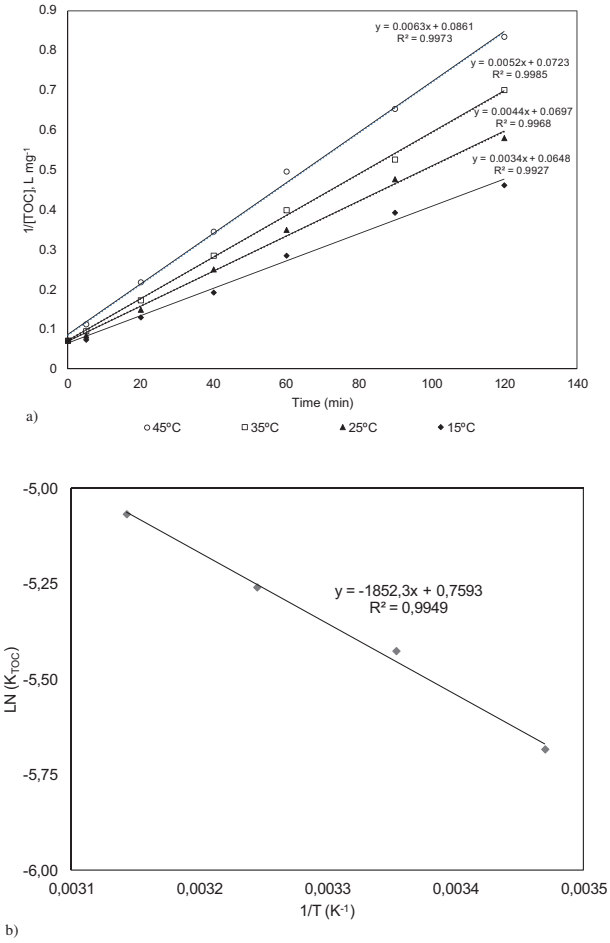

Fig. 7. Kinetic carbamazepine mineralization study in the $S_2O_8^{2-}$/US/UV/Fe^{2+}/H_2O_2 system. (a) Plot of a pseudo-second-order kinetic model; (b) Arrhenius plot demonstrating the temperature dependence of the mineralization rate constants, k_{TOC}. Experimental conditions: $[TOC]_0 = 14\,mg\,L^{-1}$; $[Fe^{2+}]_0 = 5\,mg\,L^{-1}$; $[H_2O_2]_0 = 100\,mg\,L^{-1}$; $[S_2O_8^{2-}]_0 = 300\,mg\,L^{-1}$; pH 2.8; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81×10^{-6} Einstein s^{-1}.

(at the four studied temperatures) that can be used to obtain the rate constant (from the slope of the graph). In addition, the linear regression correlation coefficient values (R^2) are shown in this figure. It was concluded that the mineralization of the carbamazepine solution by persulfate simultaneously activated using US, UV-C, Fe^{2+}, and H_2O_2 could be evaluated by using a pseudo-second-order kinetic model. The pseudo-first-order kinetic model was evaluated (data not shown) but resulted in a poor fit (R^2 below 0.5 in all experiments).

Fig. 7a shows that the reaction temperature positively affected the mineralization of the carbamazepine solution. When the temperature increased from 15 to 45 °C, the pseudo-second-order kinetic constant (k_{TOC}) increased from 0.0034 to 0.0063 $L\,mg^{-1}\,min^{-1}$. As shown in Fig. 7b, the thermally activated reaction corresponds with the Arrhenius equation ($\ln(k_{TOC}) = \ln(A) - Ea/RT$). In this case, higher temperatures generate a greater number of sulfate or hydroxyl radicals and result in faster carbamazepine mineralization in solution. This result verifies that persulfate can be thermally activated. By using the Arrhenius equation, the pseudo activation energy (Ea) was calculated as 15.4 kJ/mol. This result indicates that higher temperatures are beneficial for the mineralization reaction when using this system based on persulfate with multiple activators.

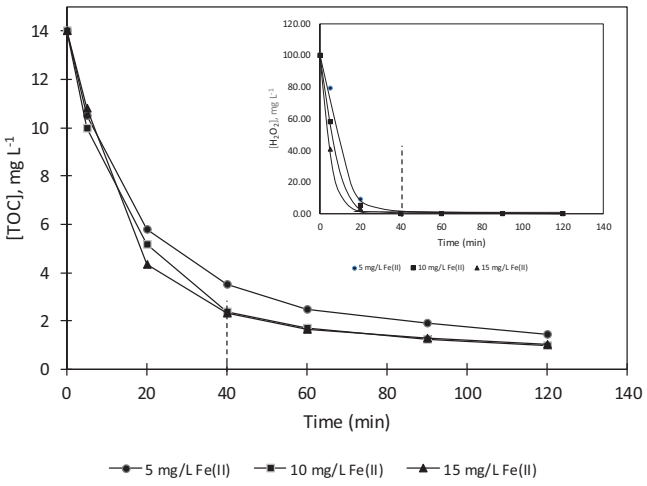

Fig. 8. (a) Effects of the initial Fe^{2+} concentration on the mineralization of the carbamazepine in solution in the $S_2O_8^{2-}$/US/UV-C/Fe^{2+}/H_2O_2 system. (b) Remaining hydrogen peroxide concentrations in solution when using different ferrous iron concentrations. Experimental conditions: $[TOC]_0 = 14\ mg\ L^{-1}$; $[H_2O_2]_0 = 100\ mg\ L^{-1}$; $[S_2O_8^{2-}]_0 = 300\ mg\ L^{-1}$; pH 2.8; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81×10^{-6} Einstein s^{-1}.

3.4. Effects of the initial Fe^{2+} concentration

Fig. 8 shows the effects of the initial Fe^{2+} concentrations (5, 10, and 15 mg L^{-1}) on carbamazepine mineralization in solution in a system using persulfate that is simultaneously activated by US, UV-C, Fe^{2+}, and H_2O_2. This reaction was conducted under the following conditions: $[S_2O_8^{2-}]_0 = 300\ mg\ L^{-1}$, $[H_2O_2]_0 = 100\ mg\ L^{-1}$, temperature = 35 °C, pH 2.8, and using ultrasound and UV-C light, as indicated above. A gradual increase in the %TOC removal from 89.8% to 92.6% (residual TOC: 1.4 and 1.1 mg L^{-1}, respectively) occurred when the $[Fe^{2+}]_0$ increased from 5 to 10 mg L^{-1}. Obviously, this increase in the initial ferrous iron concentration could produce more sulfate ($SO_4^{\bullet-}$, from persulfate activation by Eq. (13)) and hydroxyl radicals (from the Fenton reaction (Eq. (15)) in addition to the ultrasonically generated H_2O_2 and the H_2O_2 added to the solution at the beginning of the reaction. By contrast, the Fe–$(OOH)^{2+}$ complex formed by Eq. (25) can be decomposed into Fe^{2+} and hydroperoxyl radicals ($HO_2^{\bullet}$) by ultrasonic irradiation (Eq. (26)), and Fe^{2+} is formed again from the reaction of Fe^{3+} with hydroperoxyl radicals, as shown in Eq. (27) [46].

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{–}(OOH)^{2+} + H^+ \quad (25)$$

$$Fe\text{–}(OOH)^{2+} +))) (ultrasound) \rightarrow Fe^{2+} + HO_2^{\bullet} \quad (26)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad (27)$$

Next, the re-formed Fe^{2+} could react with H_2O_2 again as described in the above equations and establish a closed catalytic cycle. In addition, these results indicated that the greater Fe^{2+} concentration (15 mg L^{-1}) resulted in a greater degree of mineralization during the first 40 min of the reaction. Following 40 min, the hydrogen peroxide was totally consumed (see insert image of Fig. 8), and no further improvements were observed. Thus, the reactions described in Eqs. (15), (25)–(27) did not occur, and the excess Fe^{2+} ions would reduce the available sulfate and hydroxyl radical contents, as shown in the competitive reactions Eqs. (28) and (29), respectively [34,46].

$$Fe^{2+} + SO_4^{\bullet-} \rightarrow Fe^{3+} + SO_4^{-} \quad (28)$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad (29)$$

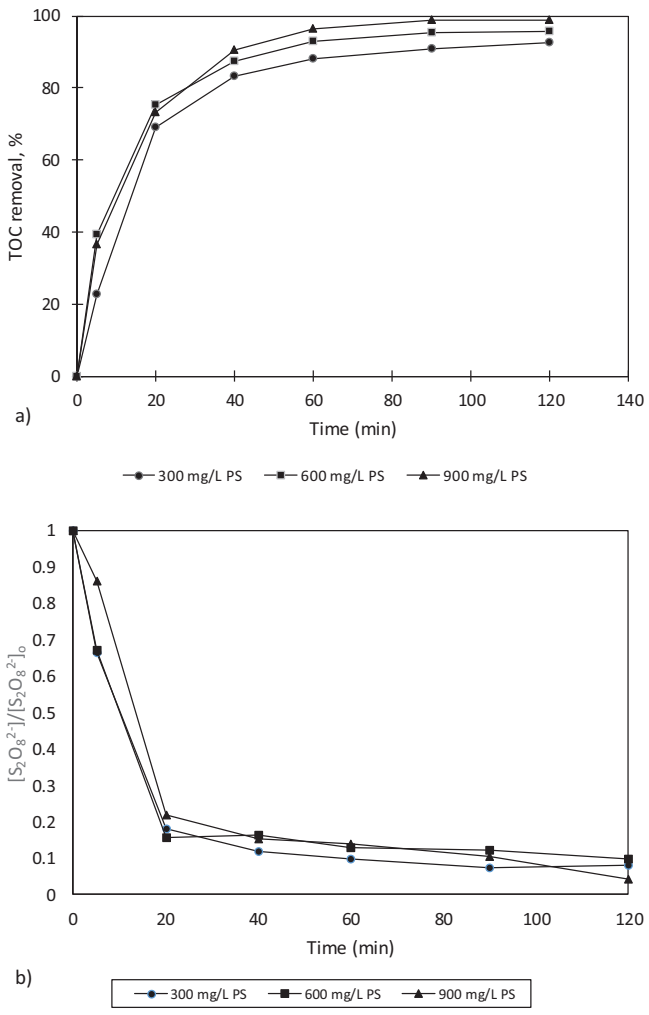

Fig. 9. (a) Effects of the initial $S_2O_8^{2-}$ concentration on the mineralization of carbamazepine in solution in the $S_2O_8^{2-}$/US/UV-C/Fe^{2+}/H_2O_2 system. (b) Remaining $S_2O_8^{2-}$ concentration in solution as a function of its initial concentration. Experimental conditions: $[TOC]_0 = 14\ mg\ L^{-1}$; $[Fe^{2+}]_0 = 5\ mg\ L^{-1}$; $[H_2O_2]_0 = 100\ mg\ L^{-1}$; temperature = 35 °C; pH 2.8; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81×10^{-6} Einstein s^{-1}.

3.5. Effects of the initial persulfate concentration

Fig. 9a shows the effects of the initial $S_2O_8^{2-}$ concentration (300, 600, and 900 mg L^{-1}) on the mineralization of the carbamazepine solution in the system using persulfate simultaneously activated by US, UV-C, Fe^{2+}, and H_2O_2. The reaction was conducted using $[Fe^{2+}]_0 = 15\ mg\ L^{-1}$, $[H_2O_2]_0 = 100\ mg\ L^{-1}$, temperature = 35 °C, pH 2.8, and ultrasound and UV-C light, as indicated above. When the initial $S_2O_8^{2-}$ concentration increased from 300 to 900 mg L^{-1} the mineralization degree increased from 92.6 to 99% (the TOC removal value reached in 90 min), which indicates that a significant amount of sulfate radicals was generated by $S_2O_8^{2-}$ activation. However, the similar $S_2O_8^{2-}$ abatement curves observed in Fig. 9b in which the initial persulfate concentration increased from 300 to 900 mg L^{-1}, could be explained by two processes, (a) the occurrence of an unproductive $S_2O_8^{2-}$ decomposition reaction (with no generation of $SO_4^{\bullet-}$) and (b) the excess sulfate radicals reduction according to Eqs. (18) and (19), as indicated above.

3.6. Investigation of the free radical mechanism in the $S_2O_8^{2-}$/US/UV-C/Fe^{2+}/H_2O_2 system

During the reaction including persulfate simultaneously activated by US, UV-C, Fe^{2+}, and H_2O_2, sulfate and hydroxyl radicals

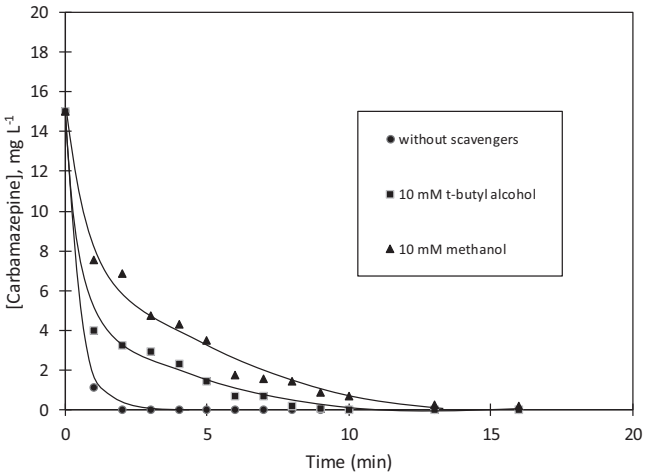

Fig. 10. Carbamazepine degradation in the absence or presence of hydroxyl and sulfate radical scavenging agents, such as *tert*-butyl alcohol and methanol, in the $S_2O_8^{2}$/US/UV-C/Fe^{2+}/H_2O_2 system. Experimental conditions: $[TOC]_0 = 14\ mg\ L^{-1}$; $[Fe^{2+}]_0 = 5\ mg\ L^{-1}$; $[H_2O_2]_0 = 100\ mg\ L^{-1}$; $[S_2O_8^{2-}]_0 = 300\ mg\ L^{-1}$; pH 2.8; temperature = 35 °C; pH 2.8; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81×10^{-6} Einstein s^{-1}; and [*tert*-butyl alcohol/methanol] = 10 mM.

could be the main oxidizing species formed according to the equations indicated above. To explain the probable contributions of these radicals in this system, the initial carbamazepine degradation was evaluated in the absence and presence of appropriate quenchers of $HO^{\bullet}$ and $SO_4^{\bullet-}$. Quenching studies were performed by adding radical scavengers, such as *tert*-butyl alcohol and methanol. *tert*-Butyl alcohol reacts 1000-fold faster with $HO^{\bullet}$ radicals ($k = (3.8–7.6) \times 10^8\ M^{-1}\ s^{-1}$) than with $SO_4^{\bullet-}$ radicals ($k = (4.0–9.1) \times 10^5\ M^{-1}\ s^{-1}$) when selectively scavenging $HO^{\bullet}$, and methanol reacts approximately 80-fold faster with hydroxyl radicals than with sulfate radicals ($k = 9.7 \times 10^8\ M^{-1}\ s^{-1}$ and $k = 1.1 \times 10^7\ M^{-1}\ s^{-1}$, respectively) [47,48]. Thus, $HO^{\bullet}$ radicals could be identified by adding excess *tert*-butyl alcohol under the same operating conditions. Furthermore, the role of $SO_4^{\bullet-}$ could be evaluated by adding excess methanol and comparing the different degradation efficiencies of carbamazepine. Fig. 10 shows the carbamazepine abatement under the following operating conditions: $[TOC]_0 = 14\ mg\ L^{-1}$; $[Fe^{2+}]_0 = 5$ and $15\ mg\ L^{-1}$; $[H_2O_2]_0 = 100\ mg\ L^{-1}$; $[S_2O_8^{2-}]_0 = 300\ mg\ L^{-1}$; pH 2.8; temperature = 25 °C; ultrasound amplitude = 100%; UV-radiation intensity = 7.81×10^{-6} Einstein s^{-1}; and [*tert*-butOH/methanol] = 10 mM. In this case, the rate of carbamazepine degradation in the absence of scavengers was remarkably higher (carbamazepine was completely removed in 2 min) than in their presence because $HO^{\bullet}$ and $SO_4^{\bullet-}$ radicals were both involved in the degradation reaction. Different scavenging rates were observed for carbamazepine degradation when the reaction was performed using 10 mM *tert*-butyl alcohol (carbamazepine completely removed in 9 min) or 10 mM methanol (carbamazepine was completely removed in 16 min). Sulfate radicals were the main oxidant species when *t*-butyl alcohol was added (inhibited $HO^{\bullet}$) because the reaction was slower than in the case without scavengers. In contrast, both radicals were inhibited when using methanol, which resulted in slower degradation. However, carbamazepine degradation was not fully inhibited. It could be probably due to the following reasons: no excess of scavengers was used or other processes such as UV-C (it would not require $HO^{\bullet}$ or $SO_4^{\bullet-}$ radicals) might be unaffected by the presence of scavengers. Fig. 11a shows the remaining hydrogen peroxide and dissolved oxygen concentrations during the reactions in the absence or presence of radical scavengers. The consumption of H_2O_2 was slower in the presence of *tert*-butyl alcohol or methanol, potentially due to a decrease in

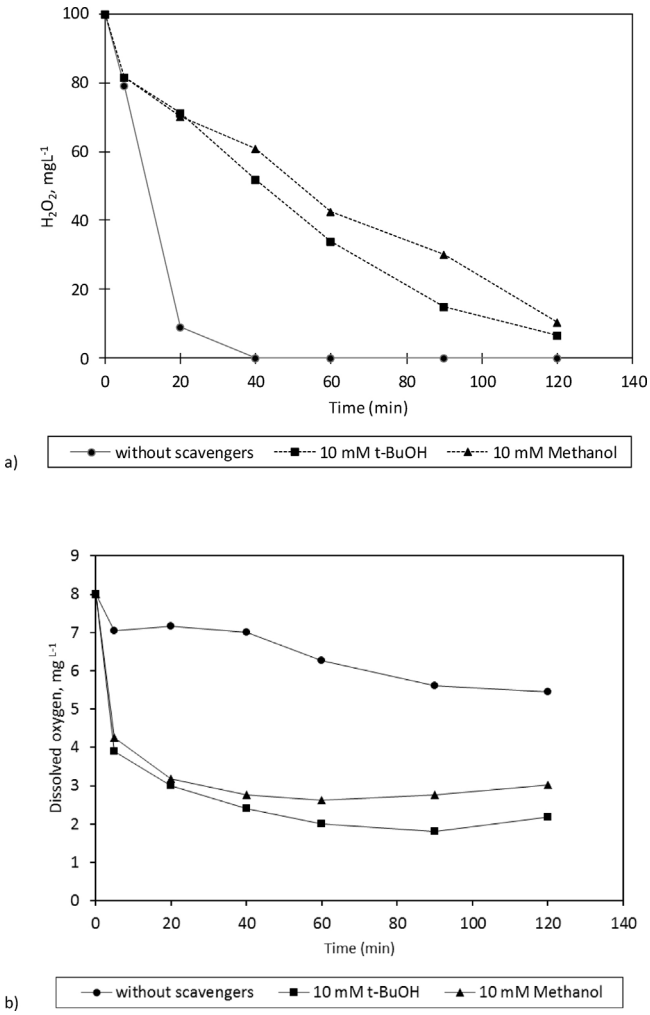

Fig. 11. Remaining hydrogen peroxide and dissolved oxygen concentrations in the absence or presence of hydroxyl and sulfate radical scavenging agents, such as *tert*-butyl alcohol and methanol in the $S_2O_8^{2}$/US/UV/Fe^{2+}/H_2O_2 system. Experimental conditions: $[TOC]_0 = 14\ mg\ L^{-1}$; $[Fe^{2+}]_0 = 5$ and $15\ mg\ L^{-1}$; $[H_2O_2]_0 = 100\ mg\ L^{-1}$; $[S_2O_8^{2-}]_0 = 300\ mg\ L^{-1}$; pH 2.8; temperature = 35 °C; pH 2.8; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81×10^{-6} Einstein s^{-1}; and [*tert*-butyl alcohol/methanol] = 10 mM.

the availability of hydroxyl radicals in solution, which results in a lower hydrogen peroxide consumption from its reaction with $HO^{\bullet}$ radicals (Eq. (30)). Methanol and *tert*-butyl alcohol react either with $HO^{\bullet}$ radicals according to Eqs. (31) and (32), respectively, or with $SO_4^{\bullet-}$ radicals according to Eqs. (33) and (34), respectively [49]. By contrast, a decrease in the dissolved oxygen concentration in scavenging systems was observed relative to the scavenger free reaction (see Fig. 11b) because oxygen can participate in another series of reactions, such as the formation of peroxy radicals from methanol/*tert*-butyl alcohol radicals (according to Eqs. (35) and (36)) [50,51].

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (30)$$

$$HO^{\bullet} + CH_3OH \rightarrow H_2O + CH_2OH \quad (31)$$

$$HO^{\bullet} + (CH_3)_3COH \rightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O \quad (32)$$

$$SO_4^{\bullet-} + CH_3OH \rightarrow SO_4^{2-} + {}^{\bullet}CH_2OH + H^+ \quad (33)$$

$$SO_4^{\bullet-} + (CH_3)_3COH \rightarrow H^+ + SO_4^{2-} + {}^{\bullet}CH_2(CH_3)2COH \quad (34)$$

$${}^{\bullet}CH_2OH + O_2 \rightarrow {}^{\bullet}O_2CH_2OH \quad (35)$$

$${}^{\bullet}CH_2(CH_3)_2COH + O_2 \rightarrow O_2CH_2(CH_3)_2COH \quad (36)$$

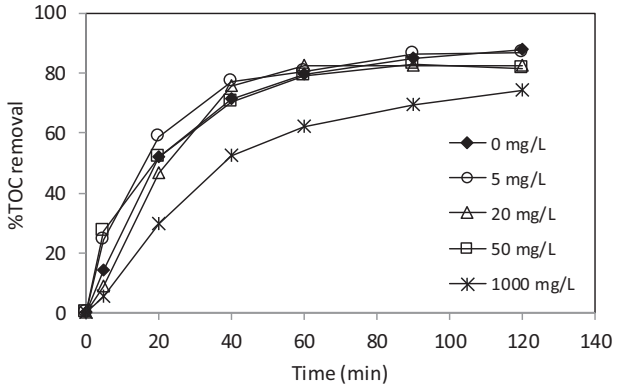

Fig. 12. The effects of the initial NaCl concentration on the mineralization of the carbamazepine solution in the PS/US/UV/Fe^{2+}/H_2O_2 system. Experimental conditions: $[TOC]_0$ = 14 mg L^{-1}; $[Fe^{2+}]_0$ = 5 mg L^{-1}; $[H_2O_2]_0$ = 100 mg L^{-1}; $[S_2O_8{}^{2-}]_0$ = 300 mg L^{-1}; pH 2.8; temperature = 35 °C; pH 2.8; ultrasound amplitude = 100%; and UV-C radiation intensity = 7.81 × 10^{-6} Einstein s^{-1}.

3.7. Effects of chloride ions

Various inorganic ions may coexist with carbamazepine in some waters and affect the mineralization reaction. Chloride is a main constituent in aqueous environments. Thus, it is important to study the effects of chloride because it reacts with hydroxyl and sulfate radicals. The mineralization reaction was studied by adding different concentrations of NaCl salt (5, 20, 50, and 1000 mg L^{-1}) to the carbamazepine solution at the beginning of the reaction in the $S_2O_8{}^{2-}$/US/UV-C/Fe^{2+}/H_2O_2 system at 25 °C. These results are shown in Fig. 12 and indicate that the mineralization degree achieved in the absence or presence of chloride was similar at small chloride concentrations and slightly decreased when the chloride concentration was 1000 mg L^{-1} (87.7% (without NaCl), 83% (20 mg L^{-1} NaCl), 82% (50 mg L^{-1} NaCl), and 75% (1000 mg L^{-1})). Chloride might have two opposite effects in this reaction. First, Cl^- could react with sulfate and hydroxyl radicals according to Eqs. (37)–(39) to generate weaker species, such as chlorine atoms, Cl, or dichloride radicals, $Cl_2{}^{\bullet-}$, decreases the availability of $SO_4{}^{\bullet-}$, and $HO^\bullet$ radicals in solution [52,53]. Second, Cl and $Cl_2{}^{\bullet-}$ could generate new hydroxyl radicals according to Eqs. (40)–(42) [54]. Thus, the radical activity in the presence of these chloride concentrations is still significant.

$$SO_4{}^{\bullet-} + Cl^- \rightarrow Cl + SO_4{}^{2-} \quad (37)$$

$$Cl + Cl^- \rightarrow Cl_2{}^{\bullet-} \quad (38)$$

$$HO^\bullet + Cl^- \rightarrow Cl + HO^- \quad (39)$$

$$Cl + H_2O \rightarrow HO^\bullet + HCl \quad (40)$$

$$Cl_2{}^{\bullet-} + H_2O \rightarrow HO^\bullet + 2Cl^- + H^+ \quad (41)$$

$$Cl_2{}^{\bullet-} + HO^- \rightarrow HO^\bullet + 2Cl^- \quad (42)$$

4. Conclusions

The results demonstrated that the in situ chemical oxidation process using persulfate simultaneously activated by US/UV-C/Fe^{2+}/H_2O_2 is a potential alternative for controlling water pollution caused by emerging contaminants, such as carbamazepine (%TOC removal 99% in 90 min). Sulfate electrolytes (added as $FeSO_4{\cdot}7H_2O$) would inhibit the coalescence of cavitation bubbles and increase the sulfate radical concentrations formed from sono-ferrous-activated persulfate. In addition, Fe^{2+} would be regenerated through photo-reduction of the $Fe(OH)^{2+}$ complex. Under acidic conditions, Fe^{2+} can exhibit catalytic effects on H_2O_2 decomposition and persulfate activation. Extra hydroxyl radicals would be formed in the photo-Fenton reaction. The mineralization of carbamazepine in solution can be evaluated by using a pseudo-second-order kinetic model. Excess Fe^{2+} ions can reduce the availability of sulfate and hydroxyl radicals. With excess persulfate, an unproductive $S_2O_8{}^{2-}$ decomposition reaction (with no generation of $SO_4{}^{\bullet-}$) or a rapid reaction between excess sulfate radicals to produce sulfate anions could occur. Hydroxyl and sulfate radicals were major oxidant species involved in the mineralization reaction. In the presence of 1000 mg L^{-1} chloride, the radical activity was still significant (75% of initial solution TOC removed).

Acknowledgments

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References

[1] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Water Res. 41 (2007) 1013–1021.
[2] P.H. Roberts, K.V. Thomas, Sci. Total Environ. 356 (2006) 143–153.
[3] I. Sires, E. Brillas, Environ. Int. 40 (2012) 212–229.
[4] M.J. Benotti, R.A. Trenholm, B.J. Vanderford, J.C. Holady, B.D. Stanford, S.A. Snyder, Environ. Sci. Technol. 43 (2009) 597–603.
[5] X. Hu, J. Yang, C. Yang, J. Zhang, Chem. Eng. J. 161 (2010) 68–72.
[6] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Croiss, Water Res. 39 (2005) 4797–4807.
[7] J.P. Bound, K. Kitsou, N. Voulvoulis, Environ. Toxicol. Pharmacol. 21 (2006) 301–307.
[8] V. Pererira, K. Linden, H. Weinberg, Water Res. 41 (2007) 4413–4423.
[9] T. Saji, S.M. Chandra, A. Ashutosh, P. Saroy Kumar, J. Pharm. Biomed. Anal. 56 (2011) 423–428.
[10] P. Braeutigam, M. Franke, R.J. Schneider, A. Lehmann, A. Stolle, B. Ondruschka, Water Res. 46 (2012) 2469–2477.
[11] G. Vernouiller, P. Eullaffroy, A. Lajeunesse, C. Blaise, F. Gagné, P. Juneau, Chemosphere 80 (2010) 1062–1068.
[12] Y.T. Lin, C.J. Liang, J.H. Chen, Chemosphere 82 (2011) 1168–1172.
[13] I.M. Kolthoff, A.I. Medalia, H.P. Raaen, J. Am. Chem. Soc. 73 (1951) 1733–1739.
[14] M.G. Antoniou, A.A. Cruz, D.D. Dionysiou, Appl. Catal. B: Environ. 96 (2010) 290–298.
[15] W.S. Chen, Y.C. Su, Ultrason. Sonochem. 19 (2012) 921–927.
[16] L. Hou, H. Zhang, X. Xue, Sep. Purif. Technol. 84 (2012) 147–152.
[17] D. McDowell, M. Huber, M. Wagner, U. Von Gunten, T.A. Ternes, Environ. Sci. Technol. 39 (2005) 8014–8022.
[18] S. Chiron, C. Minero, D. Vione, Environ. Sci. Technol. 40 (2006) 5977–5983.
[19] D. Vogna, R. Marotta, R. Andreozzi, A. Napolitano, M. díIschia, Chemosphere 54 (2004) 497–505.
[20] J. Deng, Y. Shao, N. Gao, S. Xia, C. Tan, S. Zou, X. Hu, Chem. Eng. J. 222 (2013) 150–158.
[21] A. Bernabeu, S. Palacios, R. Vicente, R.F. Vercher, S. Malato, A. Arques, A.M. Amat, Chem. Eng. J. 198 (2012) 65–72.
[22] A. Karpinska, A. Sokól, J. Karpinska, J. Pharm. Biomed. Anal. (2015), http://dx.doi.org/10.1016/j.jpba.2014.06.033.
[23] C. Martínez, M. Canle, M.I. Fernández, J.A. Santaballa, J. Faria, Appl. Catal. B: Environ. 102 (2011) 563–571.
[24] N. Tran, P. Drogui, F. Zaviska, S.K. Brar, J. Environ. Manage. 131 (2013) 25–32.
[25] A. Ghauch, H. Baydoun, P. Dermesropian, Chem. Eng. J. 172 (2011) 18–27.
[26] D.P. Mohapatra, S.K. Brar, R.D. Tyagi, P. Picard, R.Y. Surampalli, Sci. Total Environ. 447 (2013) 280–285.
[27] A. Jelic, I. Michael, A. Achilleos, E. Hapeshi, D. Lambropoulou, S. Pérez, M. Petrovic, D. Fatta-Kassinos, D. Barcelo, J. Hazard. Mater. 263P (2013) 177–186.
[28] Q. Zhang, J. Chen, C. Dai, Y. Zhang, X. Zhou, J. Chem. Technol. Biotechnol. (2014), http://dx.doi.org/10.1002/jctb.4360.
[29] J. Deng, Y. Shao, N. Gao, Y. Deng, S. Zhou, X. Hu, Chem. Eng. J. 228 (2013) 765–771.
[30] M.M. Ahmed, S. Chiron, Water Res. 48 (2014) 229–236.
[31] Y.F. Rao, L. Qu, H. Yang, W. Chu, J. Hazard. Mater. 268 (2014) 23–32.
[32] A.J. Gordon, R.A. Ford, The chemistís companion, in: A Handbook of Practical Data, Techniques and References, A Wiley Interscience Publication, New York, 1972.
[33] C. Liang, C.F. Huang, N. Mohanty, R.M. Kurakalva, Chemosphere 73 (2008) 1540–1543.
[34] C.J. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Chemosphere 55 (2004) 1213–1223.
[35] A.G. González, J.M. Santana-Casiano, N. Pérez, M. González-Davila, Environ. Sci. Technol. 44 (2010) 8095–8101.
[36] B. Neppolian, A. Doronila, F. Crieser, M. Ashokkumar, Environ. Sci. Technol. 43 (2009) 6793–6798.
[37] V. Pereira, K. Linden, H. Weinberg, Water Res. 41 (2007) 4413–4423.

[38] C.J. Liang, H.W. Su, Ind. Eng. Chem. Res. 48 (2009) 5558–5562.
[39] D. Salari, N. Daneshvar, A. Niaei, S. Aber, M.H. Rasoulifard, J. Environ. Sci. Health Part A 43 (2008) 1–7.
[40] M.L. Crimi, J. Taylor, Soil Sediment Contam. 16 (2007) 29–45.
[41] Y.H. Tsang, Y.H. Koh, D.L. Koch, J. Colloids Interface Sci. 275 (2004) 290–297.
[42] X. Zou, T. Zhou, J. Mao, X. Wu, Chem. Eng. J. 257 (2014) 36–44.
[43] C. Liang, C.P. Liang, C. Chen, J. Contam. Hydrol. 106 (2009) 173–182.
[44] A. Stefansson, Environ. Sci. Technol. 41 (2007) 6117–6123.
[45] H. Benkelberg, P. Warneck, J. Phys. Chem. 99 (1995) 5214–5221.
[46] A. Ghauch, H. Baydoun, P. Dermesropian, Chem. Eng. J. 172 (2011) 18–27.
[47] R. Matta, S. Tlili, S. Chiron, S. Barbati, Environ. Chem. Lett. 9 (2011) 347–353.
[48] G.P. Anipsitakis, D.D. Dionysiou, Environ. Sci. Technol. 38 (2004) 3705–3712.
[49] R. Matta, S. Tlili, S. Chiron, S. Barbati, Environ. Chem. Lett. 9 (2011) 347–353.
[50] K.D. Asmus, H. Möckel, A. Henglein, J. Phys. Chem. 77 (1973) 1218–1221.
[51] W.J. Cooper, C.J. Cramer, N.H. Martin, S.P. Mezyk, K.E. OíShea, C.V. Sonntang, Chem. Rev. 109 (2009) 1302–1345.
[52] R.X. Yuan, S.N. Ramjaun, Z.H. Wang, J.S. Liu, J. Hazard. Mater. 196 (2011) 173–179.
[53] P. Caregnato, J.A. Rosso, J.M. soler, A. Arques, D.O. Mártire, M.C. González, Water Res. 47 (2013) 351–362.
[54] C. Tan, N. Gao, Y. Deng, W. Rong, S. Zhou, N. Lu, Sep. Purif. Technol. 109 (2013) 122–128.